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Study of the Growth Parameters Involved In Synthesizing Boron Carbide Filaments

Second Quarterly Report

by

A. Gatti
C. Mancuso

December 1964

Prepared for National Aeronautics and Space Administration

under Contract NASw 937

Space Sciences Laboratory
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I. SUMMARY

This quarterly report is the second progress report of a study sponsored by NASA on Contract NASW-937. The program is concerned with: (1) the synthesis of B_4C whiskers, (2) the characterization of these whiskers in terms of their chemical and physical properties at room and elevated temperatures, and (3) the utilization of such whiskers in composites.

In a recent study[1] it was determined that vanadium was an effective catalyst which markedly increased both the quantity and size of B_4C whiskers grown. Materials of similar activity to vanadium as determined by the periodic table were studied during this period. It was found also that molybdenum was an effective catalyst.

Another important growth parameter which is the geometry of the growth chamber, was investigated. The various components comprising the growth area were optimized as to their effect on growth of B_4C whiskers. These studies have led to a ten-fold increase in the yield of B_4C whiskers, and will be described in this report. The results of additional studies on the surface perfection of B_4C whiskers is also presented.

The apparatus for tensile testing of B_4C whiskers at elevated temperatures has been designed and built, and is currently being assembled.

Composites of B_4C-epoxy and B_4C-aluminum were fabricated. The aluminum composites specimens were tested in tension at room temperature, and the strengths were of the order of 14,000 psi. Some composites which contained Fernico "5" as the matrix were also tested.

Future work will include further studies of the growth process, and a continuing material characterization program. The tensile properties of individual B_4C whiskers at elevated temperatures will be measured. Composite fabrication will be emphasized during the following period with the goal of studying the strength behavior of such composites at elevated temperatures.

II. INTRODUCTION

The purpose of this program is to synthesize boron carbide whiskers, to ascertain their mechanical properties, and to utilize such whiskers as reinforcing media in metals and resins. Whiskers could qualify as exceptional reinforcing material since individual strength measurements of whiskers can be as high as 3×10^6 psi [2]. The successful utilization of such strong crystals should lead to a new class of high strength, high temperature composites capable of increasing by an order of magnitude the present capability of our strongest materials.

This progress report describes a continued effort to study the growth parameters which affect B_4C whisker production with the view towards understanding the growth phenomena and the optimization of growth conditions. Such efforts have led to studies of the geometry of the whisker growth chamber, which have resulted in an order of magnitude increase in whisker production.

Further studies have been conducted on effective catalysts which can control the size and number of B_4C whiskers. It appears that both vanadium and molybdenum are an effective catalyst.

Additional electron microscopic studies have been made on the state of perfection of B_4C whiskers. Also, more small composites of B_4C epoxy and B_4C aluminum have been fabricated. The apparatus for testing individual whiskers at high temperatures has been designed and built, and equipment will be described in this report.

III. EXPERIMENTAL PROCEDURES AND RESULTS

A. GROWTH STUDIES

1. Description of Equipment

Growth studies were performed during this reporting period in a graphite resistance furnace which has been used throughout the contract period. Some changes have been made in the deposition area which has led to significant enhancement of whisker growth. These results will be described in Section A-3.

2. Catalytic Studies

The catalytic effect of vanadium on whisker growth was reported previously[1]. Other metals, specifically those close to vanadium in the periodic table could possibly also have a beneficial effect on the growth of B_4C whiskers because of chemical, structural, physical, etc., similarity. To date titanium, chromium, and molybdenum have been tried under identical conditions as those used for the vanadium studies[1]. Chromium and titanium do not appear to affect the growth of B_4C whiskers to any significant degree. Molybdenum, however, has a beneficial effect similar to that observed with vanadium. Figure 1A is a photograph of an "exhausted"* run before a molybdenum addition while Figure 1B is a run to which molybdenum has been added. A definite increase in B_4C whiskers can be noticed. At least two further metal additions will be tried, namely, zirconium and niobium.

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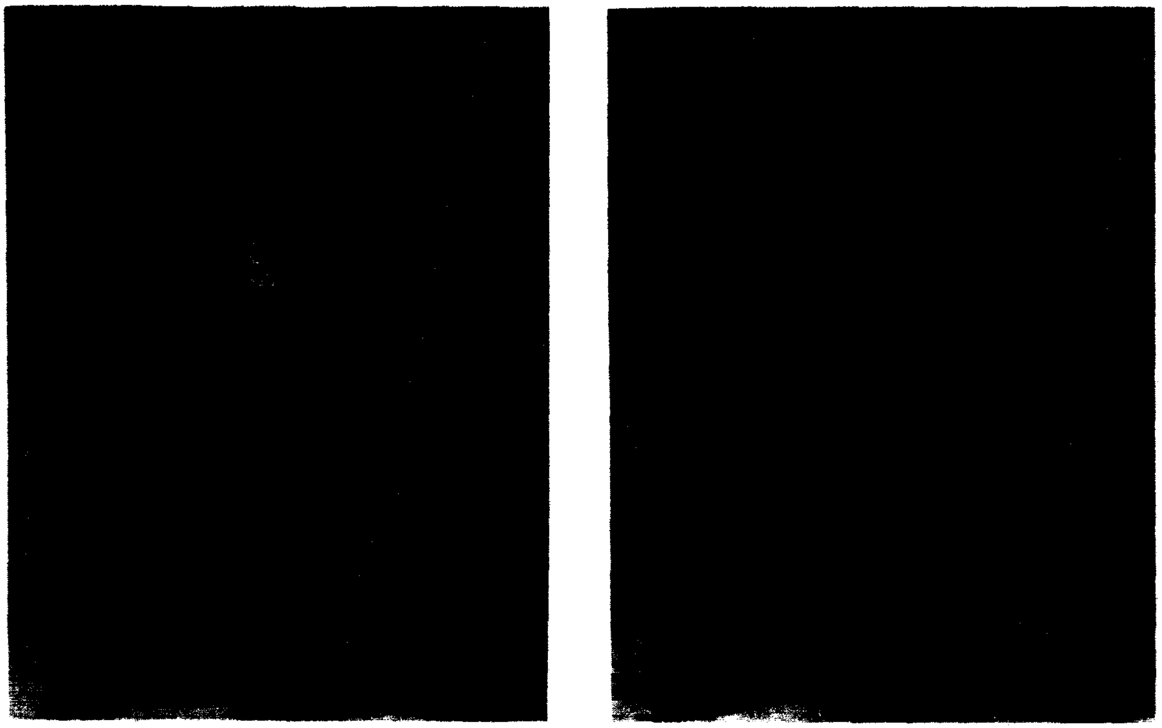
* It has been noted previously[1] that continual re-use of 'as-received' bulk B_4C powder would gradually become catalytically exhausted after repeated growth runs so that eventually the growth of B_4C whiskers would cease.



(a) (b)

Figure 1. (a) "Exhausted" Run Before Molybdenum Addition (About 1/2 Size)
(b) "Exhausted" Run After Molybdenum Addition (About 1/2 Size)

3. Geometric Conditions Affecting Growth

A major effort has been expended in order to optimize the various parameters which can influence the growth of B_4C whiskers so that greater yields of high strength whiskers can be produced. The catalytic effect of vanadium and molybdenum and possibly other metal vapors on the growth of B_4C whiskers was one approach.

Another parameter, the geometry of the whisker growth area, was also studied during this reporting period. Since most geometric conditions can affect either the chemical gradient of the vapor available for deposition or the supersaturation of the vapor itself, this geometric parameter is an important variable which deserves consideration.

It was assumed that vapor species present in the deposition area were essentially under molecular flow conditions due to the operating pressure (about 50 microns vacuum). Thus, the deposition mandrel surface was influencing a hollow cylinder-like volume of active vapor, which was about 1-1/2" in outside diameter (the I. D. of the mandrel itself) by about 1 cm in depth as evidenced by whisker lengths produced. The core-volume of vapor (about 1 inch in diameter) was essentially being pumped out of the system and wasted. It was decided to attach an additional deposition surface to the "Lazy Susan"[3] tray arrangement in order to possibly utilize this center portion of vapor which was escaping. Figure 2 shows how such an attachment was made. The additional mandrel (a) is a hollow graphite can one-half inch in diameter and four inches long with a 11/16 hole drilled into the bottom as a mounting device for fastening the mandrel to the center rod of the "Lazy Susan". The mandrel was purposely hollowed out in order to minimize any effect on the temperature gradient originally present. An improvement in both the number and the quality of B_4C whiskers was noted. One additional modification was then made. It was further deduced that a baffle above the deposition zone would locally decrease the pumping rate and thereby effectively increase the supersaturation of vapor at the deposition site. The baffle, which was in the form of a graphite disc 1/8" thick of sufficient diameter to slide through the deposition tube (approx. 1-1/2" dia.) perforated with four 1/4" holes, was

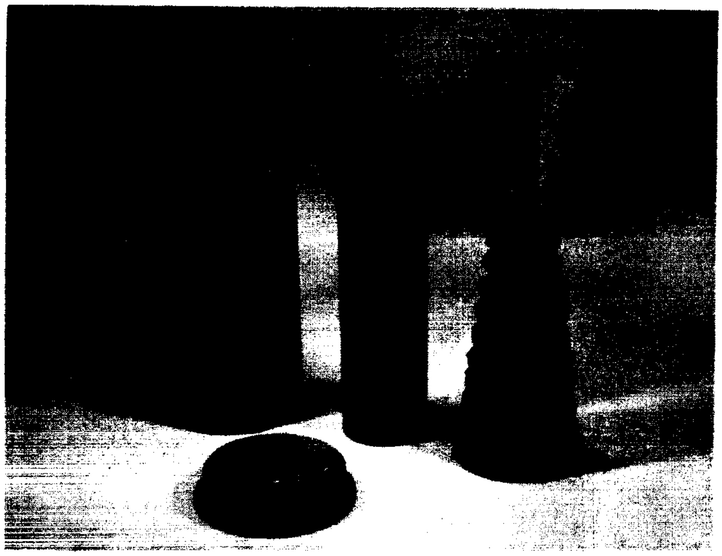


Figure 2. Photograph Showing Additional Mandrel Added to Top of "Lazy Susan" Tray (About 1/3 Size)

placed in the deposition mandrel. The top of the center hollow mandrel held the baffle in position. This geometric configuration resulted in a ten-fold increase in yield of B_4C whiskers. Figure 3A and 3B illustrates these results. Figure 3A depicts a typical run before an internal mandrel and baffle, while 3B shows a typical run with the internal mandrel and baffle added. Notice that the growth area has expanded to include nearly all available deposition surfaces, which is about 4" in length compared to about 1" in the former arrangement.

Additional modification of the geometry of the growth zone may be further beneficial and will be further studied.

B. MECHANICAL PROPERTIES OF B_4C WHISKERS

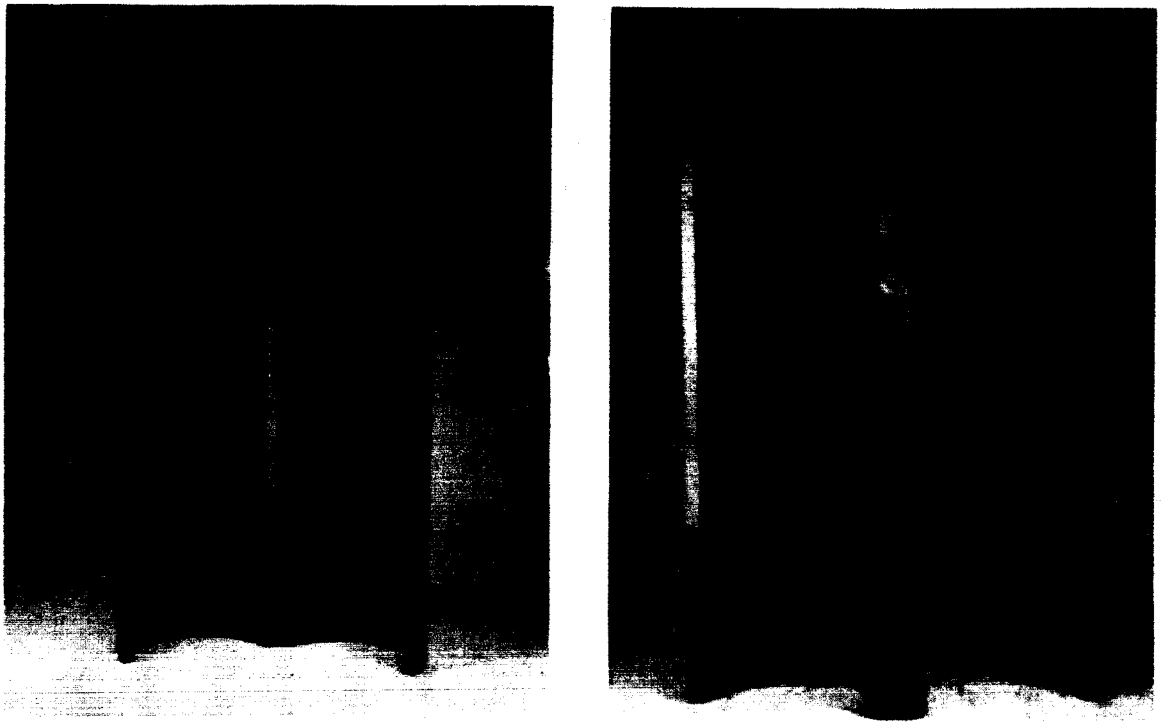
1. High-Temperature Bend Tests of B_4C Whiskers

An apparatus has been designed and built in order to perform both room and elevated temperature bend tests on B_4C whiskers. Initially, room temperature tests will be performed, and if the apparatus perform properly, a microfurnace will be wound for the purpose of conducting the high temperature tests.

The apparatus is based on the type used by Pearson, Read, and Feldmann(4) and is shown schematically in Figure 4. The purpose of the cantilever spring is to act as a load attenuator, since the anticipated bending loads are too small to be measured directly by the Instron. An auxiliary telescope can be mounted in the system to measure the specimen deflection. Presently, strain gages are being mounted on the cantilever spring. During the next report period, the system should be operable.

C. CRYSTAL AND MORPHOLOGICAL CHARACTER OF B_4C WHISKERS

Further studies have been conducted on the surface perfection of B_4C whiskers. A discussion of surface perfection and its anticipated effect on whisker strength was made earlier(1).



(a) (b)

Figure 3. (a) Typical Run Before the Internal Mandrel and Baffle Additions (About 1/2 Size)
(b) Typical Run After Mandrel and Baffle Additions (About 1/2 Size)

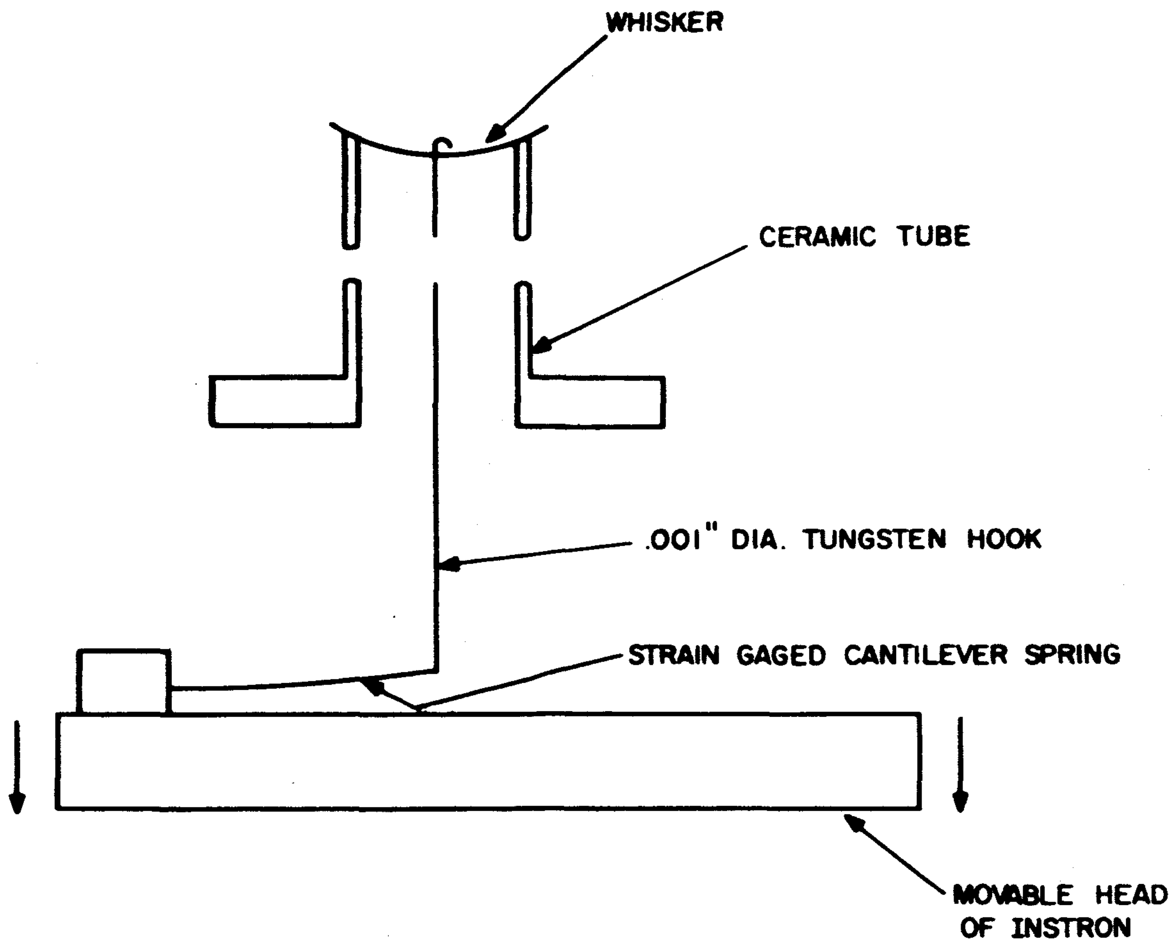


Figure 4. Schematic Diagram of Individual Whisker Testing Apparatus

Figures 5A and 5B show examples of B_4C whisker surfaces which would not be expected to exhibit high strengths due to the overgrowths and steps on their surfaces. Since very high magnifications are necessary to make such defects visible, techniques must be developed for sorting out only the stronger (more perfect) whiskers so that the full strength potential of whisker-containing composites can be achieved. Roughened surfaces of the whiskers also add to the difficulty of packing whiskers to high volume fractions utilizing the present techniques. As long as smooth surfaces are available, whiskers can slide past one another so that they can be densely compacted. Such behavior is noticed while packing alumina whiskers(5) whose long lengths and smooth surfaces are easily ascertained. Thus far, the B_4C whiskers have been packed to fractions equivalent to 10 volume percent of the composite. Techniques are being devised which will combat and minimize these problems.

D. COMPOSITE STUDIES

It was felt that a variety of matrix materials which could survey the feasibility of reinforcing potential of B_4C whiskers should be studied. Thus, by selecting a process which takes into account such variables as the melting point, wetting ability, and ease of fabrication(3), three materials have been utilized: 1) PJ122 epoxy to represent resinous composites, 2) aluminum to represent light weight medium temperature applications, and 3) Fernico "5"* to study high temperature applications.

During present reporting period considerable emphasis was placed on composite fabrication. Considerable difficulty was encountered while attempting to fabricate both aluminum and Fernico "5" composites because of poor infiltration of the matrix metal into the whisker bundles. Epoxy-based composites will be fabricated in the near future.

* Fernico "5" is a G. E. Alloy containing 46% iron, 26% nickel, and 26% cobalt.

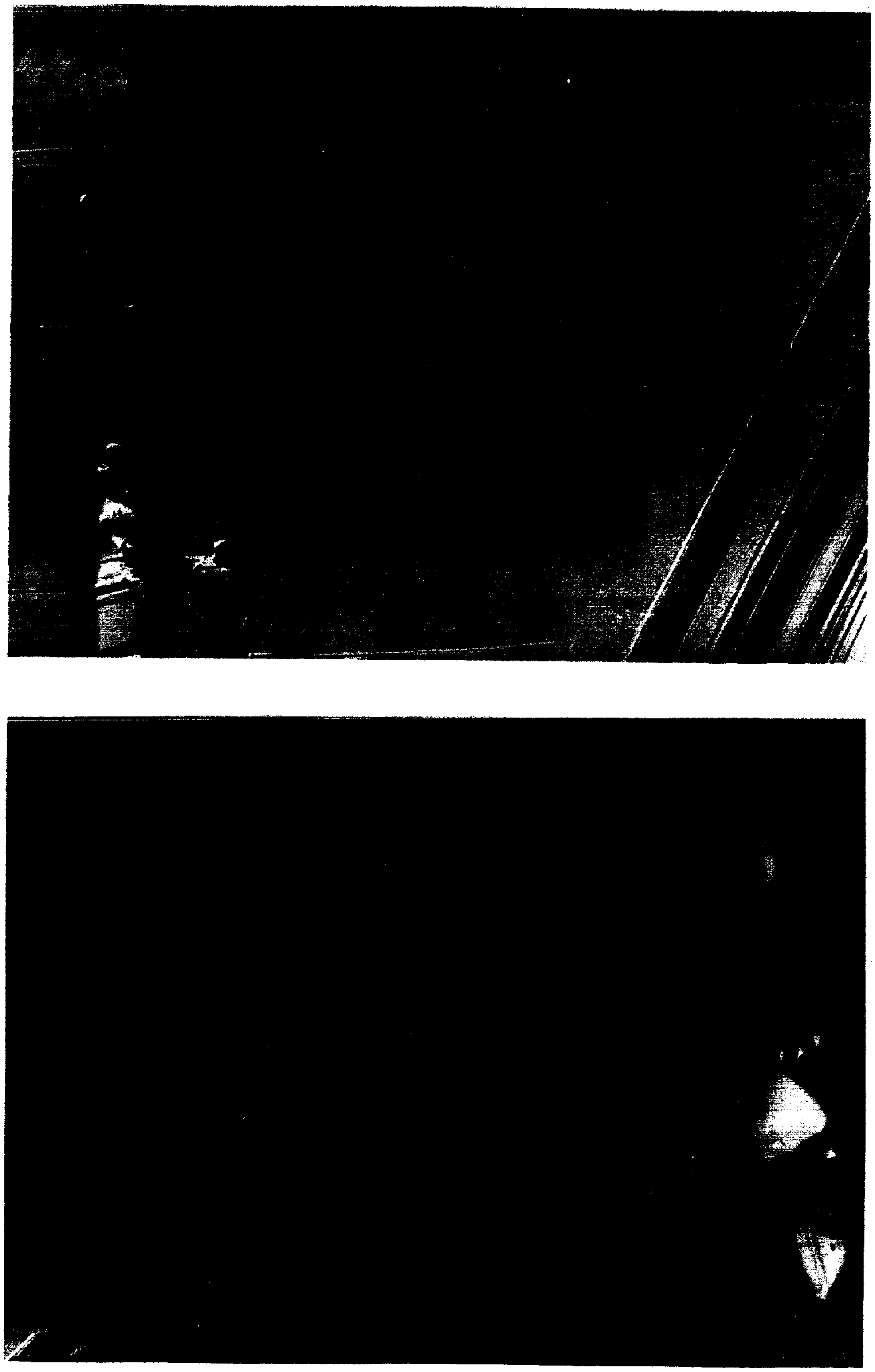


Figure 5. Electron Micrograph Showing Overgrowths on the Surface in B_4C Whiskers (Mag. 25,000X)

1. Fernico "5" Composites

Previous attempts to fabricate Fernico "5" - B_4C composites[1] were hampered both by gas evolution during the melt-down process and by whisker dissolution during impregnation. Both of these limitations have now been minimized. Boron added to the Fernico "5" charge was beneficial in slowing down whisker dissolution while a change in impregnation technique has eliminated the gas evolution problem. It was discovered that if the system outside the capillary tube was kept under vacuum while the upper portion of the capillary itself was closed off after the pump-down phase, then any evolved gas after the metal was molten travelled toward the capillary instead of blowing molten metal upward as was formerly observed[1].

The ability to control the above mentioned difficulties has led to a final problem yet to be solved. Fused silica capillaries packed with B_4C whiskers are used as molds to contain the molten Fernico "5" alloy. The difficulty now lies in forcing the alloy through the packed whisker bundle which requires a significant pressure. Thus far, due to the pressure required for impregnation and due to the high temperature necessary to keep the Fernico "5" alloy molten, the fused silica capillaries have consistently failed. Techniques which can reinforce the capillaries or resorting to more refractory mold materials are presently being contemplated.

2. Aluminum Composites

Most attempts to fabricate aluminum B_4C composites were not successful during this reporting period. However, it is felt that the difficulties encountered can be solved by refinement of the technique presently used[1]. A major problem is the reaction of the molten aluminum with the fused silica capillary molds. It has been recently observed that a finite time of contact between molten aluminum and B_4C whiskers is necessary before wetting and impregnation occurs. This is presumably due to a surface reaction between Al and B_4C whiskers since wetting does not occur immediately on direct contact. Such a time factor is necessary for the removal of adsorbed gases or films originally present on the surface of the B_4C whiskers. Because of this phenomena, molten aluminum attack of the fused silica capillaries occurs if the impregnation time is long. Such techniques as rapid impregnation were unsuccessful since the Al metal would pass completely through the whisker bundle without reaction or wetting. Techniques such as metallic coatings to promote more rapid wetting will be tried in order to minimize this problem. Other mold materials will be utilized if they prove successful for the Fernico "5" composites. Two composites, which were partially infiltrated, were tested and exhibited tensile strengths of 14,000 psi.

IV. CONCLUSIONS N65-23210

Continued contributions to the technology of growing B_4C whiskers was made. It was discovered that the element molybdenum, in addition to vanadium, would enhance the yield and size of individual B_4C whiskers. Powder additions of molybdenum, when added to exhausted B_4C powder (powder which would no longer grow whiskers), also showed an equal or better growth of B_4C whiskers than the best B_4C bulk powder used to date using the pure vapor method. An addition has been written to the patent disclosure describing the vanadium experiments.

Geometric studies have also significantly added to B_4C whisker growth technology. Whisker growing processes, in general, produce only small volumes of usable whiskers for a given run. Thus, additives which can increase whisker yields are most useful. The geometric changes made in the whisker growth chamber have resulted in greater than an order of magnitude increase in whisker yield. A patent docket has been written to document this latest discovery.

Author

In the future studies more emphasis will be placed on the successful utilization of B_4C whiskers in composite materials. Thus emphasis will be placed on several problems to be solved, such as 1) Capillary or mold problems, and 2) High packing fraction of whiskers in the composites.

V. FUTURE WORK

Future work will include further studies of geometric effects in the growth of B_4C whiskers using the pure vapor method. Also dynamic process studies will be pursued with the objective of further testing catalytic additions and growth optimization.

Structure studies concerned with the degree of perfection of B_4C whiskers will continue.

The apparatus for testing individual B_4C whiskers at high temperatures has been built, so that strength tests will be performed in the near future.

Further composite studies are contemplated with special emphasis being placed on solving the mold problems and on the refinement of present techniques.

ACKNOWLEDGEMENTS

Acknowledgement is given to Messrs. W. Laskow, C. Miglionico and R. Mehan for their valuable assistance in this program.

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